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Obtained from Multiphoton Ionization
of Atoms in Strong Fields**


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**Interpretation of Electron Spectra Obtained from
Multiphoton Ionization of Atoms in Strong Fields**

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Electron energy distributions in multiphoton ionization experiments show several peaks, which correspond to the absorption of several photons more than needed to ionize the atom. We will show that this reflects the distribution of atomic excitation at the time the electrons are emitted. The broadening and shift of the electron spectra measures the shift of the initial-to-final-state energy difference caused by the strong field. Outgoing channels with low energy electrons become closed at high fields; new "continuum-bound" electronic states appear. These states may have a chaotic motion.

The energy spectrum of electrons emitted by atoms irradiated with strong laser fields has shown unexpected structures (Fabre et al. 1982, Kruit et al. 1983a, Johann et al. 1985, and references therein, Rhodes 1985). When the laser field is just strong enough to make detectable electrons, the electron energy is closely equal to the difference in energy between N_m photons absorbed and the ionization energy of the atom, where N_m is the minimum number of photons needed for ionization; see e.g. Fig. 5b of Kruit et al. (1983). When the laser intensity is raised further, additional peaks appear, corresponding to the absorption of $N_m + S$ photons and the emission of an electron, leaving the ion in its ground state. This was quickly named "above threshold ionization". At even higher laser intensity the electron energy peaks broaden and shift somewhat, and the lowest energy peak actually disappears. After an initial bewilderment, some papers were written to explain these results: Mittleman (1984a,b), Muller et al. (1983), Muller and Tip (1984). Some of them made unrealistic assumptions, (the atom moving adiabatically into a pulsed laser field); others have given correct explanations, but under very restrictive, and somewhat unreal conditions, (a zero range potential and circularly polarized photons), and also using very complex arguments.

In this publication we will show how fundamental principles can be used to clarify the meaning of the features of the measured electron energy distribution, and how to get valid conclusions from these measurements. It will be seen that our statements are model-independent and we will determine the limits of their validity. Also, we will review some terms that seem to get obfuscated by some of the literature: AC Stark shift, ponderomotive force, the shift of the ionization potential, and continuum-continuum transitions.

We will try to distinguish three situations, illustrated in Figs. 1, a,b,c. In a), an atom is in a strong electromagnetic field, which is interacting with it. In b), an electron is emitted, and it is far enough from the residual ion that their interaction is negligible, but both the electron and the ion are still in the same e.m. field as the atom was in a). In c), the electron is detected and its energy is measured in a region where the e.m. field is zero. In quantum mechanics, the uncertainty principle limits our ability to distinguish among these situations, and therefore it limits the validity of such descriptions. There is no difficulty with c), as the detection of the electron occurs very far from the interaction region. In order to distinguish a) and b), we have to be able to construct a wave packet that describes a free electron emitted from an atom and close enough to it in space and time that the e.m. field is almost the same as it was before its emission; we will discuss both the space and time limitations.

The electromagnetic field amplitude and phase are always uniform in space over a distance of order λ , its wavelength and over a time $\tau_{em} = 1/\Delta\omega_{em}$ where $\Delta\omega_{em}$ is its spectral bandwidth. [In the following, factors of order unity will always be neglected.] In order to make things simple, we will first assume that the field is monochromatic enough that its variation is negligible over the time of interest. Localization of the electron wave packet within λ causes its translational momentum to be uncertain by $\Delta p_T = \hbar / \lambda$, corresponding to an uncertainty of its translational energy by $\Delta \mathcal{E}_T / \mathcal{E}_T = 2 \Delta p_T / p_T$. In order to produce a wave packet, we have to demand that $\Delta \mathcal{E}_T / \mathcal{E}_T \ll 1$. This can be satisfied, if

$$\mathcal{E}_T \geq \frac{2\hbar^2}{m\lambda^2} \quad (1)$$

For $\lambda = 0.2 \mu$, this gives $\mathcal{E}_T \geq 4 \times 10^{-6}$ eV: hardly a limitation for all past experiments.

From conservation of energy and the basic principles of quantum electrodynamics, we conclude that the energy of the atom in a) and the sum of the energies of the ion and the electron can differ only by an integral number, N , of field quanta, $\hbar\omega$:

$$\mathcal{E}_D(N) \equiv \mathcal{E}_A(E) + N\hbar\omega = \mathcal{E}_{A+}(E) + \mathcal{E}_{e1}(E) \quad (2)$$

The symbols are the following: $\mathcal{E}_D(N)$ is the "dressed" energy of the initial atomic state, or the channel energy of the final state; $\mathcal{E}_A(E)$, $\mathcal{E}_{A+}(E)$ are the energy of the atom and the ion [or more generally that of the initial and final atomic state] respectively, in the electromagnetic field; $\mathcal{E}_{e1}(E)$ is the electron energy in the field. For simplicity we will assume that $\mathcal{E}_D(N)$ is less than the double ionization threshold; therefore only a single electron can be present. It is important to note that the atom and ion have internal degrees of freedom, while the electron has none (except spin). Therefore $\mathcal{E}_A(E)$, $\mathcal{E}_{A+}(E)$ are continuous functions of the field intensity, their E dependence determines the (possibly non-linear) susceptibility, α , by the formula $\mathcal{E}_A(E) = \mathcal{E}_A(0) + \alpha(E, \omega)E_0^2$, where $E = E_0 \cos \omega t$. These are adiabatic energies; they are referenced to the atomic and ionic ground state energies, $\mathcal{E}_A(0)$, $\mathcal{E}_{A+}(0)$, and they are not quantized; these energies are identical to the quasi energies of the Floquet Hamiltonian. See e.g. Zeldovich (1974), Maquet et al. (1983), Holt et al. (1983). The field dependence of the energy difference

$$\Delta \mathcal{E}_+(E) = [\mathcal{E}_{A+}(E) - \mathcal{E}_A(E)] - [\mathcal{E}_{A+}(0) - \mathcal{E}_A(0)] \quad (3)$$

is one definition of the shift of the ionization energy by the field (see discussion below). Since $\mathcal{E}_{A+}(E)$ and $\mathcal{E}_A(E)$ generally refer to tightly bound (i.e. rather unpolarizable) ground states, these AC Stark shifts are expected to be quite small.

Next we recall that a free electron cannot absorb or emit quanta, (it can only scatter them). Therefore comparing Fig. 1b with 1c, we can write

$$\mathcal{E}_{e1}(E) = \mathcal{E}_{e1}(\text{Det}) \equiv \mathcal{E}_{e1} \quad (4)$$

i.e. the electron has a well-defined energy which is the same in the field and at the detector. Compton scattering imparts an energy to the electron that can be estimated non-relativistically as

$$\frac{\Delta \mathcal{E}_{e1}}{\mathcal{E}_{e1}} = \frac{2\Delta p_{e1}}{p_{e1}} = \frac{I \sigma_{Th} \tau_{em}}{c (2\mathcal{E}_{e1} m)^{1/2}} \quad (5)$$

where $I = cE_0^2/8\pi$ is the field intensity, $\sigma_{Th} = (8\pi/3)r_c^2$ is the Thomson cross section; this is the radiation pressure. In order to estimate its magnitude, assume $I = 10^{14} \text{ W/cm}^2$, $\tau_{em} = 10^{-11} \text{ sec}$, $\mathcal{E}_{e1} = 1 \text{ eV}$, then $\Delta \mathcal{E}_{e1}/\mathcal{E}_{e1} = 4 \times 10^{-6}$; it is negligible.

Another important remark is that the number of absorbed (or stimulatedly emitted) quanta can change only while the electron is close enough to the atom that the electrostatic interaction can supply the extra momentum to the electron. This can occur classically only while the electrostatic energy of the electron is more than the photon energy, $e^2/r \geq \hbar\omega$. In addition, the effective cross section for absorption falls rapidly when the electron's energy uncertainty, $\hbar v/r$, gets less than the photon energy, $\hbar\omega$. Thus continuum-continuum transitions, discussed recently by Edwards et al. (1984),

and Deng and Eberly (1984) can occur only while the electron is very close to the atom.

Combining Eqs. (2) and (4) we get

$$\mathcal{E}_D(N) = \mathcal{E}_A(E) + N\hbar\omega = \mathcal{E}_{A^+}(E) + \mathcal{E}_{el}(\text{Det}) \quad (6)$$

or

$$\mathcal{E}_{el}(\text{Det}) = N\hbar\omega - [\mathcal{E}_{A^+}(E) - \mathcal{E}_A(E)] \quad (7)$$

In general, we don't know N , but in the experiments of Fabre et al. (1982), Kruit et al. (1983a), and Johann et al. (1985) a series of electron energies were observed, that correspond to $N = N_m + S$ where N_m is the minimum number of photons needed to ionize the atom and $S=0,1,2,\dots$. It was correctly deduced that each peak belongs to an N -photon absorption when the final state is the ground state of the ion. [In the recent experiments of Johann et al. (1985) at high photon energies and field intensities, other peaks were also observed that are associated with multiple ionization and inner shell effects.] Eq. (6) then shows that we are probing a "dressed" state whose energy is S photons higher than the ionization energy. In perturbation theory, this is described as an N_m+S photon absorption, independently for each S ; in a rate equation approximation, it corresponds to the sequential absorption of N photons. In a more general theory, the electron is emitted by an atom that is partially in a coherent state, which is a superposition of several dressed energy states, and corresponds to a "collective" motion of the electrons (Szöke 1985, Szöke and Rhodes 1985). As the simplest example, if mutual electrostatic repulsion between electrons is small, equivalent electrons in a shell all respond in the same manner to the external field.

Assuming a probability $p_N(E)dE$ of emitting an electron after N photon absorption in field E , and a field distribution $p(E(t))dVdt$, we get for the electron spectrum:

$$\begin{aligned} p(\mathcal{E}_{e1}) &= \int P_N(E)P(E(t))\delta(\mathcal{E}_{e1}(E) - \mathcal{E}_{e1})dEdVdt \\ &= \int P_N(E)P(E(t))\delta(N\hbar\omega - \mathcal{E}_{A+}(E) + \mathcal{E}_A(E) - \mathcal{E}_{e1})dEdVdt \end{aligned} \quad (8)$$

Experimentally it was shown that at high fields $p_N(E)$ is not a very strong function of N ; therefore the electron energy distribution should be similar for all $N = N_m + S$ peaks. It is determined by the distribution of Stark shifts in the focal volume, and by the possible time dependence of the e.m. field, as discussed below. This is similar to the interpretation of Stark shifts in bound state resonances by Kruit *et al.* (1983b).

In order to make further progress, let us write down explicitly the classical motion of the free electron in Fig. 1b in the electromagnetic field. From the equation of motion

$$m\ddot{x} = -eE = -eE_0 \cos\omega t \quad (9)$$

we get for the electron energy in a linearly polarized wave

$$\mathcal{E}_{e1}(E) = \bar{\mathcal{E}}_{osc} + \mathcal{E}_T = \frac{1}{4} \frac{E_0^2 e^2}{m\omega^2} + \frac{p_T^2}{2m} \quad (10)$$

where $\bar{\mathcal{E}}_{osc}$ is the average oscillating energy of the electron in the field. A quantum mechanical treatment yields similar results (Zeldovich 1975). An electron that tries to penetrate the field with less energy than $\bar{\mathcal{E}}_{osc}$ is reflected from it; this is usually called the ponderomotive potential and its

gradient, the ponderomotive force. In our discussion, we stress that the free electron is "created" in the e.m. field; therefore it follows from Eqs. (4) and (10) that it must have a minimum energy $\bar{\epsilon}_{osc}$. If we raise the field intensity, some of the low resonances in Eq. (7) may get energies that are below $\bar{\epsilon}_{osc}$ (recalling that the quantity $\epsilon_{A+}(E) - \epsilon_A(E)$ is weakly dependent on E , due to the tightly bound nature of the atomic and ionic ground state.) In this case the electron cannot escape the Coulomb potential: the open electron channel gets closed. This is a new kind of "continuum bound" state: it is in the continuum in the sense that it exists for a continuous spectrum of photon energies and it is bound in the sense that the electron cannot escape to infinity. (For a given photon energy this is a perfectly discrete state.) Our picture is thus similar to Fig. 3 of Muller and Tip (1984). The atomic radius gets very large, the electron has a classical turning point at radius R , where

$$\frac{e^2}{R} \approx N_m \hbar \omega - [\epsilon_{A+}(E) - \epsilon_A(E)] - \bar{\epsilon}_{osc} \quad (11)$$

This is a very polarizable, "floppy" atom. The "disappearance" of the lowest energy electrons was observed by Kruit et al. (1983a), Johann et al. (1985) at e.m. field intensities in good accordance with Eq. (10). Numerically we get agreement with the estimated average field of Kruit et al. (1983a), and not the peak field. It is possible that this is a sign that ionization of these (multiply excited) states is suppressed. In experiments on xenon by Johann et al. (1985), it was observed that the disappearance of an electron peak at ~ 0.7 eV (at an intensity of $\sim 2 \times 10^{14}$ W/cm²) coincided roughly with the appearance of electron spectra that indicate the presence of inner-shell excitations. Thus the "continuum bound" states may form an environment (or complex) which promotes inner shell excitation. We will try to examine this in a different paper (Szöke and Rhodes 1985).

It is clear from the preceding discussion that there are two ways to define the ionization energy (ionization potential) of an atom in an electromagnetic field. The traditional way of defining it is by the appearance of outgoing electrons; this is governed by the equation, obtainable from Eqs. (2),(10)

$$\mathcal{E}_D(N) \equiv \mathcal{E}_A(E) + N\hbar\omega = \left[\mathcal{E}_{A+}(E) + \frac{1}{4} \frac{E_0^2 e^2}{m\omega^2} \right] + \frac{p_T^2}{2m} \quad (12)$$

In first order, with $\Delta\mathcal{E}_+(E) \ll \bar{\mathcal{E}}_{osc}$ this is the limit of the Rydberg states shifted by the high frequency Stark effect (Avan et al. 1976, Liberman et al. 1983, Hollberg and Hall 1984). This is as it should be, because in the limit of high quantum numbers a Rydberg electron becomes a free electron. The second way of defining ionization is from the energy balance, Eq. (7). It should be emphasized that this latter is also a measurable quantity. Generally this will give a much smaller "AC Stark shift" than the previous one, as indeed observed in the experiments. In the region between the two energies there are states that have a classical character: the Rydberg states get mixed by the strong field and the classical motion of the electron is largely oscillatory with a superimposed slow orbital motion. Even in quantum mechanics such a state may be a chaotic one (Casati et al. 1984). Also, a very small perturbation, caused e.g. by a small change in the field, may make the orbit change drastically.

Up to now we have presented an essentially static picture; let us finally discuss the consequences of the time dependence of the electromagnetic field. There are three times in the problem: the decay time of the atom into a channel, the travel time of the emitted electron out of the potential well,

and the correlation time of the field. We argued above that as long as the outgoing electron is within the radius where it can absorb additional photons, it may be counted as an unionized atom; also we calculated that the "escape time" of the outgoing electron is of the order of the light period, therefore much shorter than the field correlation time, τ_{em} . Thus the channel energy, $\mathcal{E}_0(E)$, is always well defined. Over the much longer time that the outgoing electron travels in the ion's Coulomb field, the field may change, changing the partition of the channel energy between the electron and the residual ion. We can calculate the time, Δt , over which this coupling takes place, by equating the change in the ion's Stark shift, $\Delta \mathcal{E}_+(E)$, to the Coulomb energy at the distance, $v\Delta t$,

$$\frac{\Delta \mathcal{E}_+(E)}{\tau_{em}} \Delta t = \frac{e^2}{v\Delta t} \quad (13)$$

giving the result,

$$\Delta \mathcal{E} = \left[\frac{\Delta \mathcal{E}_+(E) e^2}{v\tau_{em}} \right]^{1/2} \quad (14)$$

For an assumed $\mathcal{E}_{e1} = 1$ eV, $\Delta \mathcal{E}_+(E) = 1$ eV, $\tau_{em} = 10^{-11}$ sec, this gives an energy shift of ~ 15 meV; much smaller than the observed one.

Let us discuss now the atomic decay time. If the atomic decay time were shorter than the field correlation time and if the photon absorption were sequential, the atom would always decay into the open channel during the risetime of the field; therefore neither "above threshold" ionization, nor the disappearance of the lowest energy electron channel would have been observed. A non-sequential photon absorption corresponds to a coherent state of the atom; the lengthening of the decay time corresponds then to the atom being in a state which is largely a non-decaying one, and only a small admixture of a

state that has an outgoing electron, (corresponding to direct photoionization). The atomic decay time that correspond to autoionization may be lengthened if the atomic excitation energy, $\mathcal{E}_0(N)$, is shared by many electrons, or if the electron collisions causing autoionization are suppressed by the external field. In a more complete theory, (Szöke 1985), we hope to estimate the relative contribution of these processes.

In Eq.(2) we assumed that the energies of the atom and the ion in the field depend adiabatically on the instantaneous value of the latter; this is true for a slowly varying field. In fact, as discussed above, the atom's decay time into the ionization channel is observed to be longer than the field correlation time, τ_{em} . In this case the state of the residual ion after the electron leaves can be a non-linear function of the field history. In Szöke (1985) a time dependent Hartree-Fock theory is expanded beyond the adiabatic approximation, using a two-time formalism. The first correction term gives a dependence on the value of the field and its first derivative. This may account for the observed electron spectrum that has a broadening, but very little shift, at high values of the e.m. field.

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Figure Caption

Fig. 1. Three steps in the measurement of the electron energy spectrum in (multiphoton) photoionization.

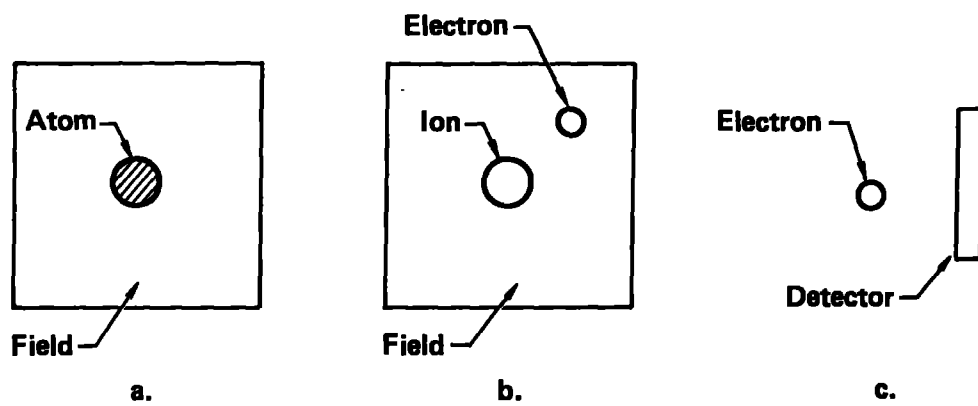


Figure 1.